

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

in

Thermo and Fluid Dynamics

**Experimental Study of Using Butanol or  
Octanol Blends as Alternative Fuels in Diesel  
Engines**

TANKAI ZHANG

Department of Applied Mechanics  
CHALMERS UNIVERSITY OF TECHNOLOGY  
Gothenburg, Sweden, 2016

**Experimental Study of Using Butanol or Octanol Blends as Alternative  
Fuels in Diesel Engines**

TANKAI ZHANG

© TANKAI ZHANG, 2016

THESIS FOR LICENTIATE OF ENGINEERING no 2016:05

ISSN 1652-8565

Department of Applied Mechanics  
Chalmers University of Technology  
SE-412 96 Gothenburg  
Sweden  
Telephone +46 (0)31 772 1000

Chalmers Reproservice  
Gothenburg, Sweden 2016

## Abstract

With the increased travel demand, the consumption of fossil fuels, as the main energy source for transportation, has risen sharply over the last few decades. Fossil fuels are considered a non-renewable resource. In addition, burning them in internal combustion engines can generate a large amount of greenhouse gas (GHG) emissions. According to the life-cycle assessment, use of renewable fuels as alternatives in diesel engines can help to dramatically reduce GHG emissions. Furthermore, the oxygen content in alcohols may help to suppress soot formation significantly. Therefore, mixing renewable alcohols in diesel fuel may offer a potential solution for reducing GHG emissions, soot emissions and fossil fuel consumption. Hence, it is important to investigate the possibility of using alcohol/diesel blends in existing diesel engines.

To reproduce the characteristics of existing engines as closely as possible, a light duty (LD) single-cylinder engine, a heavy duty (HD) single-cylinder engine and a four-cylinder LD engine were employed with production engine settings. In both types of single-cylinder engine, engine performance and emissions were studied under steady-state conditions. In the four-cylinder LD engine, the cold start behaviour of the fuels was investigated. Four alcohols were selected to mix with diesel, i.e. *n*-butanol, isobutanol, 2-ethylhexanol and *n*-octanol. These alcohols were blended separately with one of two different cetane number (CN) improvers, either hydrotreated vegetable oil or di-tertiary-butyl peroxide, in diesel fuel. The mixtures were prepared to have the same CN as diesel fuel.

With the same CN and engine settings, the alcohol/diesel blends and diesel fuel showed very similar heat release profiles. The blends generated slightly faster combustion, leading to slightly higher indicated thermal efficiency, than diesel fuel under most of the tested conditions in both types of single-cylinder engine. Soot emissions decreased sharply when changing diesel fuel to alcohol/diesel blends. Further, the *n*-butanol and 2-ethylhexanol diesel blends showed good cold start performance in the multi-cylinder LD engine.

In conclusion, the results showed that from a combustion point of view, it is possible to use renewable fuels, such as *n*-butanol, iso-butanol, *n*-octanol or 2-ethylhexanol, mixed with diesel and ignition improver in existing diesel engines without any engine modifications.



## List of publications

This thesis is based on the following papers:

- I. T. Zhang, K. Munch, I. Denbratt, “An Experimental Study on the Use of Butanol or Octanol Blends in a Heavy Duty Diesel Engine,” *SAE Int. J. Fuels Lubr.*, 8(3): 2015–24–2491, 2015.
- II. T. Zhang, L. Jacobson, C. Björkholtz, I. Denbratt, K. Munch, “Effect of Using Butanol and Octanol Isomers on Engine Performance of Steady State and Cold Start in Different Types of Diesel Engines,” manuscript submitted to the journal *Fuel* in March 2016.



## Acknowledgements

I would like to thank my supervisor Prof. Ingemar Denbratt for offering me this PhD position at Division of Combustion and guiding me with his extensive experience in the both academic and industrial field. Karin Munch, my co-supervisor, is acknowledged for her supervision and support, especially her kindly help in the fuel storage with butanol smell.

I would like to thank the people in my reference group for sharing their profound knowledge and valuable suggestions, which continually promote the project moving forward.

I would like to thank research engineers, Alf Magnusson, Anders Mattsson, Daniel Härensten, Eugenio De Benito Sienes and Timothy Benham, for their assistance in rebuilding engines and their patience with my interruption. All my colleagues at Division of Combustion are acknowledged for creating an enjoyable and cooperative working environment. I wish to thank Chengjun Du, who introduced a great university, Chalmers University of Technology, to me first time. Thanks to Gunnar Latz for his politeness and patience, especially his advice to keep my car running.

I would like to thank Elenor Norberg and Kristin Hessel for their great help when I started my new life in Sweden.

At last, I would like to thank my wife Linhan Qiu for abandoning her career and following me to Sweden. Thanks my kids Dayou and Dita for bringing me so much happiness. Thanks my parents and my parents in-law for their wholehearted support anytime anywhere.





## REPORT



## Contents

1	Introduction.....	3
1.1	Motivation.....	3
1.2	Objective.....	4
2	Background.....	5
2.1	Alternative fuels.....	5
2.2	Properties of alcohols.....	6
2.3	Use of alcohols in Diesel engines .....	7
2.3.1	Methods for introducing alcohols as fuel in Diesel engines .....	8
2.3.2	Use of alcohol/Diesel blends.....	10
2.4	CN of the fuel .....	11
2.4.1	Effect of CN on combustion.....	11
2.4.2	CN measurement.....	13
2.5	Effect of alcohol/Diesel blends on emissions .....	16
3	Experimental apparatus and methodology.....	19
3.1	Tested fuels .....	19
3.2	Tested engines.....	20
3.2.1	HD engine specifications and conditions .....	21
3.2.2	LD engine specifications and conditions .....	23
3.2.3	Multi-cylinder engine specifications and conditions .....	25
3.3	Measurement procedure.....	26
3.4	Measurement evaluation .....	27
3.4.1	Heat release rate .....	27
3.4.2	Evaluation related to changing fuel.....	28
3.4.3	Statistical analysis .....	30
4	Results.....	33

## Contents

---

4.1	Summary of Paper I .....	33
4.2	Summary of Paper II.....	34
5	Conclusions.....	35
6	Future work.....	37
	Abbreviations .....	39
	References .....	41

# 1 Introduction

## 1.1 Motivation

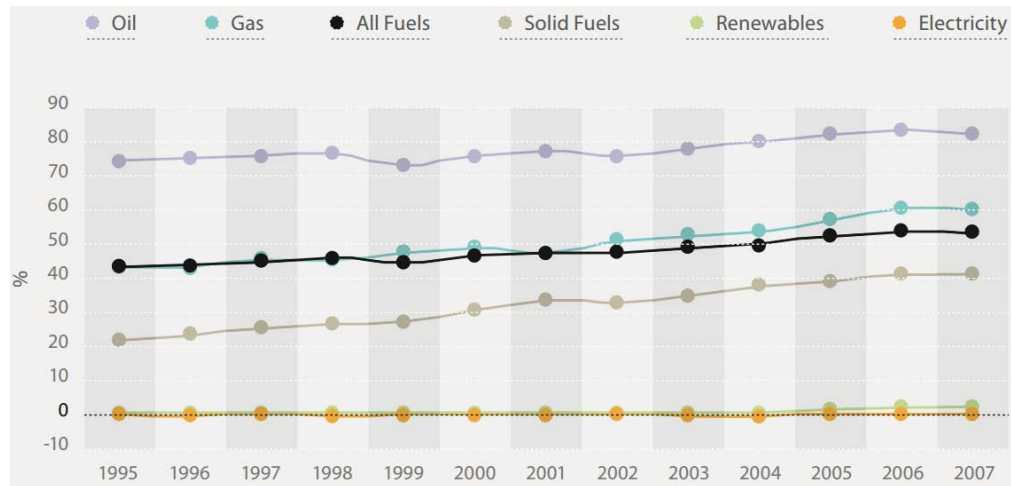
Internal combustion engines are widely applied in transportation because of their high efficiency and reliability. During the last 150 years, vehicles with internal combustion engines have facilitated people in their daily lives. However, the rise in popularity of vehicles has led to a rapid increase in fossil fuel consumption.

As a drawback of fossil fuel burning in internal combustion engines, greenhouse gas (GHG) emissions are now one of the most urgent concerns around the world owing to their effects on health and the climate. In the EU, total GHG emissions fell from 5,750 million tonnes of carbon dioxide (CO<sub>2</sub>) equivalent in 1990 to 4,611 in 2013. However, the percentage of GHG emissions generated from transport has increased from 13.7% to 19.2% during the same period.<sup>[1]</sup> In the US, transport contributed 24.6% of all GHG emissions (1551 million tonnes of CO<sub>2</sub> equivalent) in 1990 compared to 27.1% (1806 million tonnes) in 2013.<sup>[2]</sup> Thus, the share of GHG emissions from transport is still increasing in both the EU and US.

Another drawback of high levels of oil consumption relates to the contradiction between human activities and finite reserves of fossil fuels. As societies have developed, the normal life of humans has become closely dependent on the usage of fossil fuel sources. However, fossil fuels are non-renewable resources and distributed unevenly across the world. **Figure 1-1** shows the EU's import dependency of energy by sector from 1995 – 2007. The overall EU import dependency on all fuels increased by 10% over the whole time period (to 53% in 2007). Further, the dependence on imports of oil increased from 74% in 1996 to 83% in 2007. Oil reserves tend to occur in relatively concentrated pockets across the world. For instance, the eight largest oil reserve countries owned 79.4% of the proved oil reserves in the world at the end of 2014.<sup>[3]</sup>

To reduce GHG emissions and the dependence on fossil fuels, the EU has made a commitment to reduce overall GHG emissions from its 28 Member States by 20% relative to 1990 levels by 2020. At the same time, the EU also promised to increase the proportion of energy generated from renewable resources within the transportation sector to 10% by 2020 (with the overall share of energy generated from renewable sources rising to 20%). By 2030, the intent is to reduce GHG emissions by at least 40% relative to the 1990 level and for renewable sources to contribute at least 27% of all energy consumption.<sup>[4,5]</sup> However, this is an overall target and each European country has individual policies. Sweden aims to achieve a totally fossil-free vehicle fleet by 2030.<sup>[6]</sup>

In the US, the American Recovery and Reinvestment Act of 2009 stated that the share of ethanol in gasoline should be increased from 7% to 10%, and it is planned for it to remain at the latter level until 2030. <sup>[7]</sup> In Canada, a federal mandate has required 5% of the national gasoline pool to be renewable (ethanol) since 2010. <sup>[8]</sup> In addition, various provinces have stipulated equivalent or higher renewable fuel content, e.g. 5% renewable fuel in Ontario, 7.5% in Saskatchewan and 8.5% in Manitoba.



*Figure 1-1: EU-27 import dependency (in %) of energy (1995-2007) <sup>[9]</sup>*

## 1.2 Objective

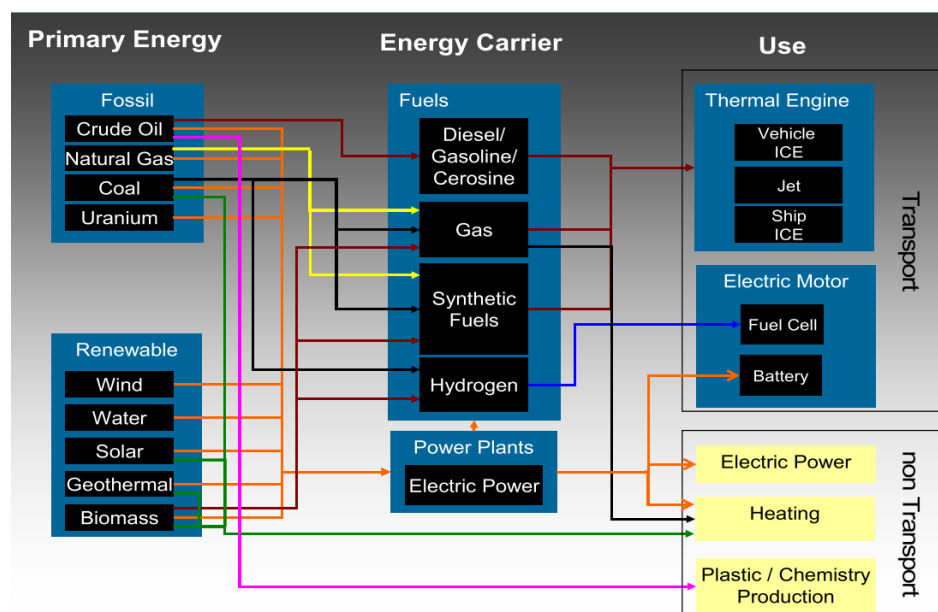
The main objective of the work described in this thesis was to investigate the possibility of using alcohol/Diesel blends coupled with ignition improver in existing engines.

It is important to evaluate the potential of partially using renewable alcohols in Diesel fuel in existing vehicles. Changing the fuel without any modification of engines could be one of the easiest and most efficient ways to increase renewable fuel use and reduce GHG emissions. In this study, *n*-butanol, isobutanol, *n*-octanol and 2-ethylhexanol were selected to blend with Diesel fuel. The cetane numbers (CNs) of the different alcohol/Diesel blends were adjusted to that of Diesel by adding two different kinds of CN improvers, i.e. hydrotreated vegetable oil (HVO) and di-tertiary-butyl peroxide (DTBP). By using the same CN for the tested fuels, ignition delay (ID) differences between the fuels could be eliminated. The experiments were performed first in a single cylinder heavy duty (HD) engine and then in a single cylinder light duty (LD) engine.

## 2 Background

### 2.1 Alternative fuels

To reduce GHG emissions and meet limits set by legislation, the use of alternative fuels in internal combustion engines may offer a good solution. Therefore, sustainable and cleaner alternative fuels have attracted considerable attention.



**Figure 2-1: Energy pathways in transport and other sectors (Source: ERTRAC)<sup>[10]</sup>**

**Figure 2-1** presents the energy pathways in different sectors. For transport, a large number of different pathways of energy supply are shown. If we focus on the use of thermal engines, the main energy carriers are Diesel/gasoline/kerosene, gas and synthetic fuels, which are all derived from crude oil, natural gas, coal or biomass. However, owing to finite reserves, as well as pollution and policy issues, alternative fuels produced from biomass may be one of the best options for use in transport. Liquid biofuels technically can be used with existing power train technologies, in some cases with minor or no technical modifications, which would facilitate a smooth market transition.

Biofuels can be produced from a wide range of biomass feedstock. Traditionally, fatty acid methyl esters, produced from rapeseed, soybean, palm oil and sunflower by an esterification process, could be used as biodiesel in Diesel engines.<sup>[11]</sup> Hydrotreated vegetable oils (HVOs) and animal fats are produced from a new process, generating a so-called second generation

renewable Diesel fuel. HVO is completely devoid of aromatics and sulphur and consists almost exclusively of straight chain and branched paraffins. <sup>[12,13]</sup> Another option is synthetic biomass to liquid (BTL), synthesized by gasification and the Fischer-Tropsch process, which is known as a third generation renewable Diesel fuel. However, the production of newer generation fuels is limited by their current high capital costs.

Bioalcohols are another type of liquid biofuel. Alcohols can be sustainably produced from sugar cane, switchgrass, potatoes, corns and other starch-rich materials by a fermentation process. In addition, alcohols can be generated from other non-food biomass lignocellulosics. Lignocellulosics mainly consist of three components: cellulose, hemi-cellulose, and lignin. One of processes for alcohol production from lignocellulosics generally involve two main steps: hydrolysis of cellulose and hemicellulose to monomeric sugars, and subsequent fermentation to produce bio-alcohol. <sup>[14,15]</sup>

## 2.2 Properties of alcohols

Some physical properties of alcohols, especially oxygen content, make them suitable candidates for Diesel engines. **Table 2-1** shows the properties of alcohols and fossil Diesel.

**Table 2-1: Properties of alcohols and Diesel** <sup>[16,17,18,19]</sup>

	Methanol	Ethanol	Isobutanol	<i>n</i> -Butanol	2-Ethylhexanol	<i>n</i> -Octanol	Diesel
Oxygen content (wt.%)	49.93	34.73	21.62	21.62	12.31	12.3	0
Density (g/ml)	0.787	0.785	0.802	0.810	0.836	0.82	0.837
Lower heating values (MJ/kg)	20.1	26.9	33.17	33.21	34.7	38.4	42.8
Cetane number	3.8	5-8	<15	17-25	27.2	37.5	52
Flash point (°C)	12	13	28	35	81	81	82
Vaporization latent heat (kJ/kg)	1109	904	566	582	-	562	270
Boiling point (°C)	65	79	108	118	184	195	210-235
Viscosity @ 40 °C (mm <sup>2</sup> /s)	0.58	1.13	2.62	2.63	5.2	5.5	3.04
Lubricity (μm)	1100	1057	-	590	-	236	315
Solubility in water	Miscible	Miscible	Immiscible	Immiscible	Immiscible	Immiscible	Immiscible

Alcohols are defined by the presence of a hydroxyl group (–OH) attached to one of the carbon atoms. The numbers of carbon atoms in alcohol molecules strongly influence their physical and chemical properties. In addition, their molecular structure has an important influence on their properties.



As the number of carbon atoms in alcohols increases, the oxygen wt.% decreases, whereas the carbon wt.% increases. A higher carbon percent usually yields a higher lower heating value (LHV), and consequently lower specific fuel consumption. The alcohols used in this study all had LHVs than Diesel fuel, which would reduce the output of the engine for the same amount of fuel injected. However, a long chain alcohol/Diesel blend is able to achieve a similar maximum output compared with Diesel fuel <sup>[20]</sup>. Straight carbon chain alcohols show slightly higher LHVs than their branched isomers.

Increasing the number of carbon atoms in alcohols reduces their molecular latent heat of vaporization but increases their boiling point and density, making their properties more similar to those of Diesel. The latent heat of vaporization influences the temperature in the cylinder after the injection, especially in the region surrounding the spray. <sup>[21]</sup> The lower density of alcohols leads to a lower energy density, which complicates their use in existing Diesel engines.

Larger alcohol molecules have a higher CN and flash point, closer to the limits specified in the EN590 Diesel standard, which would make their introduction to the market easier. Fuels with higher flash points are considered safer for distribution and storage. *n*-Octanol has a higher flash point (81 °C) than the EN590 limit of 55 °C. The CN of the fuel has a strong effect on the ID, significantly influencing the combustion behaviour.

The hydrophilicity of ethanol makes it insoluble in Diesel, and therefore it is necessary to add an emulsifier to ethanol/Diesel blends, resulting in a more complicated mixing process for preparing the fuels. The physical properties of butanol isomers and octanol isomers make them more suitable than methanol or ethanol as alternative fuels to blend with fossil Diesel.

The lubricative properties of the fuels are usually tested using a high frequency reciprocating rig to measure the wear scar diameter, which is specified in the EN590 standard with an upper limit of 460 µm. Poor lubricity may cause potential wear problems in sensitive fuel pump designs in Diesel engines. With increasing carbon atom number, alcohols show better lubricity performance; *n*-octanol is able to satisfy the EN590 limit.

In summary, larger chain alcohols (butanol isomers and octanol isomers) show properties closer to those of Diesel than smaller chain alcohols (methanol and ethanol).

## **2.3 Use of alcohols in Diesel engines**

Owing to their potential for reducing GHG emissions and sustainable methods of production, bio-alcohols are being extensively investigated as alternative fuels for internal combustion engines.

Biofuels such as alcohols can be derived from grain starches and sugar crops but also from non-food waste biomass. Waste biomass includes agricultural crop residues, such as straw and nut shells, and residues from processing, such as crude glycerine (glycerine that is not refined). Based on their life-cycle assessment, GHG emissions from burning biofuel in engines can be considered as zero. Therefore, utilizing waste bioresources to support energy for internal combustion engines offers an excellent way to achieve extremely low life-cycle GHG emissions. For instance, replacing fossil fuels with ethanol produced from wheat straw or waste wood can reduce well-to-wheels (WTW) typical GHG emissions by 80-87%.<sup>[22]</sup> Moreover, methanol or butanol produced from inedible feedstocks can also be used as alternative fuels, with potential for a substantial reduction (70% - 90%) in WTW typical GHG emissions.<sup>[22,23]</sup>

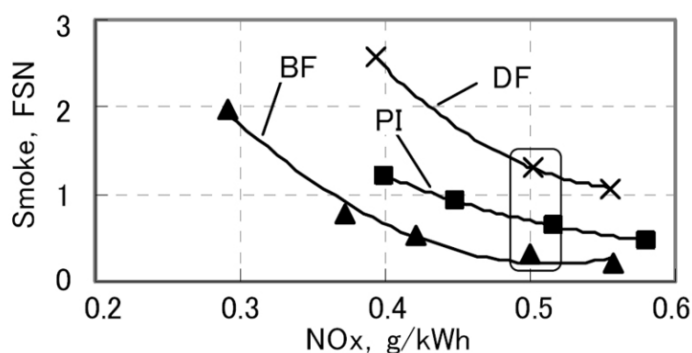
### ***2.3.1 Methods for introducing alcohols as fuel in Diesel engines***

Depending on the fuel properties and selected combustion control strategy, alcohols can be introduced into Diesel engines by three methods<sup>[24]</sup>. Firstly, alcohols and Diesel fuel can be injected using different injection systems to adjust the proportions of the fuels, and thereby control the combustion behaviour, known as the dual fuel mode.<sup>[25]</sup> Usually, a port-injector located close to the inlet valve is used to introduce alcohols. Because alcohols have poorer auto-ignition properties than Diesel, one advantage of this dual fuel system is its scope to be developed to accommodate more advanced combustion modes for future engines, such as reactivity controlled compression ignition (RCCI) or premixed compression ignition (PCI).<sup>[26]</sup> Han et al.<sup>[27]</sup> have investigated the suitability of high load operations under low temperature combustion (LTC) strategies by using Diesel, gasoline, *n*-butanol and ethanol in high compression ratio engines. They showed that by using an ethanol/Diesel dual fuel combustion strategy, the engine load can be increased to 1.65 MPa indicated mean effective pressure (IMEP) whilst complying with regulations on nitrogen oxides (NO<sub>x</sub>) and soot emissions. However, a separate injection system is required, increasing the cost and risk of maintenance.

Secondly, alcohol fumes can be introduced with the intake charge by carburetting, vaporizing or injecting, known as fumigation, whereas Diesel fuel is injected directly into the cylinder. This method is more suitable for small molecule alcohols, such as methanol and ethanol, which have good volatility. Chauhan et al.<sup>[28]</sup> and Zhang et al.<sup>[29]</sup> reported that compared with using Diesel fuel, the latter method reduces the particulate mass due to the increased oxygen content in the fuel and more premixed combustion, and increases hydrocarbon (HC) emissions because of quenching. However, the results on NO<sub>x</sub> and CO emissions were not consistent between these two papers. Ethanol fumigation has been shown to increase the volatility of particles and the amount of nucleation mode particles.<sup>[30]</sup> However, alcohol fumigation requires some engine modifications, although these are less extensive than for the dual fuel system.

Thirdly, blends of alcohol and Diesel fuel can be injected directly into the cylinder, referred to here as the blend method, requiring no hardware modification of the engine. For short carbon chain alcohols, such as methanol and ethanol, which are insoluble in Diesel fuel, an emulsifier needs to be added to promote mixing.

Chen et al. <sup>[31]</sup> have examined differences between the dual fuel mode and alcohol/Diesel blend mode in a single-cylinder Diesel engine. Port fuel injection of *n*-butanol resulted in a fuel pool in the intake and incomplete combustion, causing higher CO emissions than when using butanol/Diesel blends. In addition, the dual fuel mode generated more HC emissions because of quenching. Increased CO and HC emissions reduce the combustion efficiency, which may lead to a lower indicated thermal efficiency (ITE). **Figure 2-2** shows trade-off curves between smoke and NO<sub>x</sub> emissions for three different modes - butanol/Diesel blend direct injection (BF), butanol/Diesel dual fuel injection (PI) and Diesel direct injection (DF) - measured at 1800 rpm and 95 Nm by changing the injection timing. <sup>[32]</sup> It was found that both the dual fuel method and blended fuel method significantly improved the trade-off between smoke and NO<sub>x</sub> emissions compared to using Diesel fuel alone. Further, the blended fuel approach showed better performance than the dual fuel mode. As a result, it was concluded that the smoke reduction effect of butanol was not only due to the increased ID but also higher oxygen content of the alcohol. Butanol/Diesel blends contribute to improving the fuel spray because of the low surface tension and boiling point of butanol. However, it has also been suggested that the low CN of blends may cause problems for cold starts.



**Figure 2-2 Trade-off curves between smoke and NO<sub>x</sub> emissions (1800 rpm, 95 Nm) <sup>[32]</sup>**

Abu-Qudais et al. <sup>[33]</sup> have studied differences between the fumigation method and blend method in a single-cylinder Diesel engine with ethanol and Diesel fuel. Their results indicated that both the fumigation method and blend method generate an increase in brake thermal efficiency, CO and HC emissions, and a decrease in soot mass concentration compared with using Diesel. In addition, the fumigation method gave slightly better results than the blend

method. Similar results were reported by Şahin et al. <sup>[34]</sup> in a turbocharged automobile Diesel engine with 2-6% butanol fumed or blended with Diesel fuel. They showed that the amount of smoke generated decreased significantly when applying either of these two methods. However, the butanol fumigation method had a greater effect on smoke reduction than the blend method.

Owing to their need for engine modifications, the duel fuel mode and alcohol fumigation mode are less amenable for application in existing Diesel engines than the alcohol/Diesel blend. Therefore, the alcohol/Diesel blend method has distinct advantages for use in existing engines.

### **2.3.2 Use of alcohol/Diesel blends**

The main problem of using alcohols in Diesel engines is their LHV than Diesel fuel. However, a maximum output reduction of 4% and 3% has been measured when using Diesel blended with 30% butanol and 25% pentanol, respectively, compared to using Diesel. <sup>[35]</sup> In addition, the decrease in output is lower than the reduction in LHV of the blends. The presence of oxygen in the blends promotes complete combustion and lowers heat transfer losses. Consequently, the increased thermal efficiency of alcohol/Diesel blends partly compensates for their LHVs. However, Can et al. <sup>[36]</sup> reported that addition of 10 or 15% ethanol in Diesel fuel with emulsifier causes approximately 12.5% or 20% reduction in power, respectively, which is greater than the reduction due to the LHV and density of ethanol. Inefficient conversion of heat to work, due to a longer ID, results in the late heat release in the expansion stroke.

Rakopoulos et al. have tested a six-cylinder turbocharged Diesel engine with both ethanol/Diesel and butanol/Diesel blends <sup>[37]</sup>. The alcohol/Diesel blends showed lower soot and NO<sub>x</sub> emissions than Diesel fuel. The lower soot emissions of the blends may be explained by the presence of fuel-bound oxygen in locally rich 'zones', which seems to have a dominant influence. The same paper suggested that the reduction in NO<sub>x</sub> emissions obtained with the blends may be due to their slightly lower peak combustion temperature than Diesel. With the same level of oxygen content in the fuel, the butanol blends generated slightly higher soot emissions and slightly lower NO<sub>x</sub> emissions than the ethanol blend. Additional fundamental spray and combustion studies are required to explain this phenomenon.

Armas et al. <sup>[38]</sup> have investigated exhaust emissions after engine cold/warm starts in a turbocharged, direct injection (DI), 4-cylinder Diesel engine fuelled with an ethanol (10%)/Diesel blend or butanol (16%)/Diesel blend. Both blends displayed poor behaviour regarding NO<sub>x</sub>, HC, CO and smoke emissions under cold start conditions. The high enthalpy of vaporization of alcohols can lead to a low cylinder temperature, incomplete combustion and poor oxidation. Armas et al. <sup>[39]</sup> also studied emissions under the New European Driving Cycle with the same blends as used in their previous study. According to the results, the blends

generated lower soot and CO emissions but higher NO<sub>x</sub> and HC emissions than Diesel fuel over the total driving cycle.

In addition to their lack of need for hardware modifications, no software (engine settings) changes are necessary when applying alcohol/Diesel blends to existing Diesel engines. Replacing Diesel fuel with an alcohol/Diesel blend requires that both fuels have similar properties and combustion behaviour. Compared to methanol and ethanol, longer straight carbon chain alcohols, such as butanol and octanol, have lower latent heat of vaporization but higher LHV, CN, flash point and density, closer to those of Diesel. Furthermore, small molecule alcohols have poor solubility in Diesel fuel, which complicates their use in Diesel engines. Therefore, butanol isomers and octanol isomers are more suitable for blending with Diesel than methanol and ethanol.

## 2.4 CN of the fuel

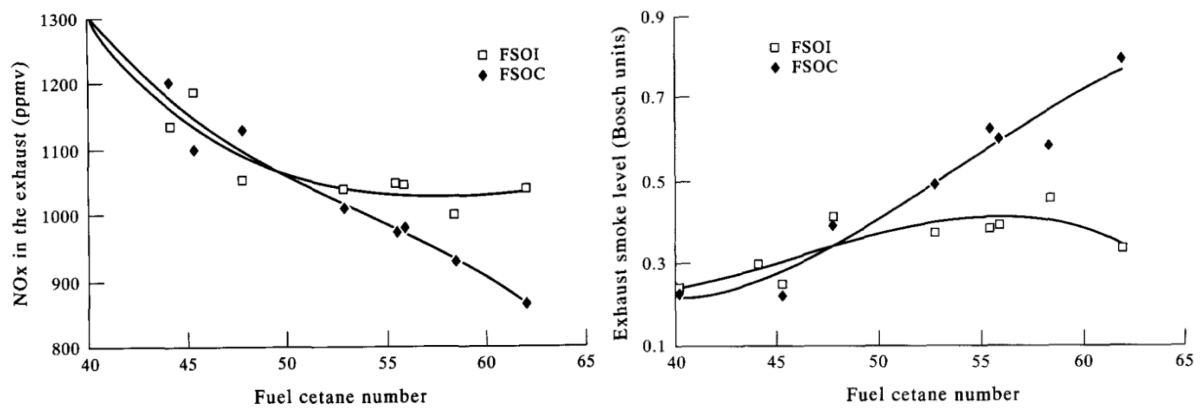
The cetane number (CN) is a dimensionless index that is related to the ID time, i.e. the period between the start of injection (SOI) and start of combustion (SOC). The CN can be used for the quantification of the ignition quality and heat release phase. Longer straight carbon chain alcohols have a higher CN than shorter ones and straight carbon chain alcohols have a higher CN than their branched chain isomers owing to the different molecule structure. However, as shown in **Table 2-1**, even *n*-octanol has a CN lower than 52, which is the low limit for European Diesel fuel specified in EN590. Therefore, to achieve similar combustion behaviour when applying alcohol/Diesel blends in production setting engines, it is desirable to adjust their CN to that of Diesel fuel.

### 2.4.1 Effect of CN on combustion

Owing to the relation between ID time and SOC, the combustion can be divided into four modes: homogeneous charge compression ignition (HCCI), premixed charge compression ignition (PPCI), partially premixed combustion (PPC), and conventional combustion. Adjusting the CN of the fuel is a potential way to switch between the PPC and conventional combustion modes <sup>[40]</sup>. For the PPC, combustion modes, changing the CN can expand or narrow the operating range. In contrast, emissions of NO<sub>x</sub>, CO and HC are relatively independent of CN but are more dependent on the ID time, which is affected by other factors, such as exhaust gas recirculation (EGR). <sup>[41]</sup>

For conventional combustion, the effect of CN on the emissions and combustion process is significant and mainly due to its influence on the ID. Ladommatos et al. <sup>[42]</sup> have investigated using Diesel fuel with CN ranging from 40.2 to 62.0 by adding ethylhexyl nitrate in the fuel as

a CN improver in a co-operative fuel research (CFR) single-cylinder Diesel engine. **Figure 2-3** shows the relation between fuel CN and NO (left) and soot (right) emissions. The tests were performed with two strategies – either fixed SOI (FSOI in the figure) or fixed SOC (FSOC). In the left plot, NO<sub>x</sub> emissions can be seen to decrease with increasing fuel CN. This can be attributed to the decreased cylinder peak temperature and percentage of fuel burned in the premixed combustion phase when the CN of the fuel was increased. In contrast, the right plot shows that soot emissions slightly increased with increasing CN, especially for a fixed SOI. On the one hand, a high CN reduces the extent of premixed combustion and fuel air mixing, which promotes the soot formation. On the other hand, a high CN fuel generates a high cylinder gas temperature, which facilitates the oxidation of soot. These two opposing factors could be responsible for the minor influence of CN on soot emissions for the FSOI strategy. HC emissions decrease with CN increase because the long ID generates an overlean fuel air mixture and increases the possibility of wall wetting, leading to increased HC formation. Similar results for the effect on emissions can be found in [43] and [44].



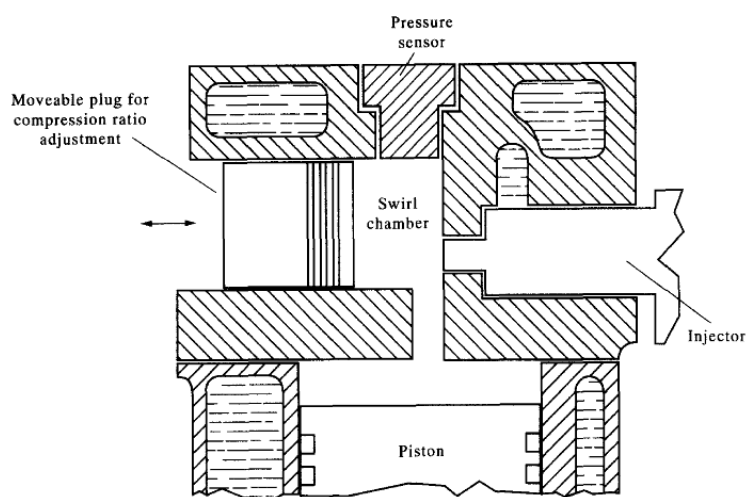
**Figure 2-3 Relation between fuel CN and NO (left) and soot (right) emissions** <sup>[42]</sup>

The injection pressure may also influence the effect of CN on emissions. <sup>[45]</sup> With a high injection pressure, soot emissions are less sensitive to variation of CN. In contrast, NO<sub>x</sub> emissions decrease with increasing CN regardless of injection pressure. Lü et al. <sup>[46,47]</sup> studied the influence of CN improver on emissions from a four-cylinder DI Diesel engine fuelled with ethanol/Diesel blends. Adding a CN improver in the blends partly counteracted their tendency to generate higher CO and HC emissions by reducing the ID, resulting in a higher combustion temperature and more complete combustion. NO<sub>x</sub> emissions were reduced further by using CN improver in the blends, whereas there was only a slight increase in soot emissions. Moreover, the brake thermal efficiency increased with increasing amount of CN improver. İçingür et al. <sup>[48]</sup> also reported that adjusting the fuel CN is an effective way to improve the combustion by reducing the ID.

## 2.4.2 CN measurement

Generally, there are four methods to measure the CN: using a CFR engine, ignition quality tester (IQT) <sup>[49]</sup>, near infra-red (NIR) analyzer or by calculating the cetane index (CI).

The CFR engine method is based on the American Society for Testing and Materials (ASTM) standard D613. This is the only direct method to measure the CN of a fuel. Therefore, the CFR engine method serves as a reference for other CN detection methods. The CFR cetane rating engine is a single cylinder, continuously variable compression ratio engine. **Figure 2-4** shows a schematic of the combustion chamber of the CFR engine. The combustion chamber is connected to a swirl chamber. On the one side of the swirl chamber, there is a movable plug, which is used to adjust the compression ratio by changing the volume of the combustion chamber. On the other side of the swirl chamber, a standard injector with a pintle-type nozzle is mounted.



**Figure 2-4 Combustion chamber of CFR engine** <sup>[42]</sup>

The CN scale is defined by two reference fuels: the long straight-chain hydrocarbon hexadecane ( $C_{16}H_{34}$ ) has good ignition quality and is assigned a CN of 100, whereas the highly branched compound 2,2,4,4,6,8,8,-heptamethylnonane (HMN, also  $C_{16}H_{34}$ ) has poor ignition quality and is assigned a CN of 15. <sup>[50]</sup> The sample fuel and reference fuels are tested under the same steady-state conditions. When the sample fuel has the same ID and compression ratio as a mixture of the two primary reference fuels, its CN can be calculated from the volume percentage of the two components of the reference fuel as follows:

$$CN = P_{hex} + 0.15 \cdot P_{HMN} \quad (2.1)$$

where  $P_{hex}$  and  $P_{HMN}$  are the percentage hexadecane and HMN content in the reference fuel mixture, respectively.

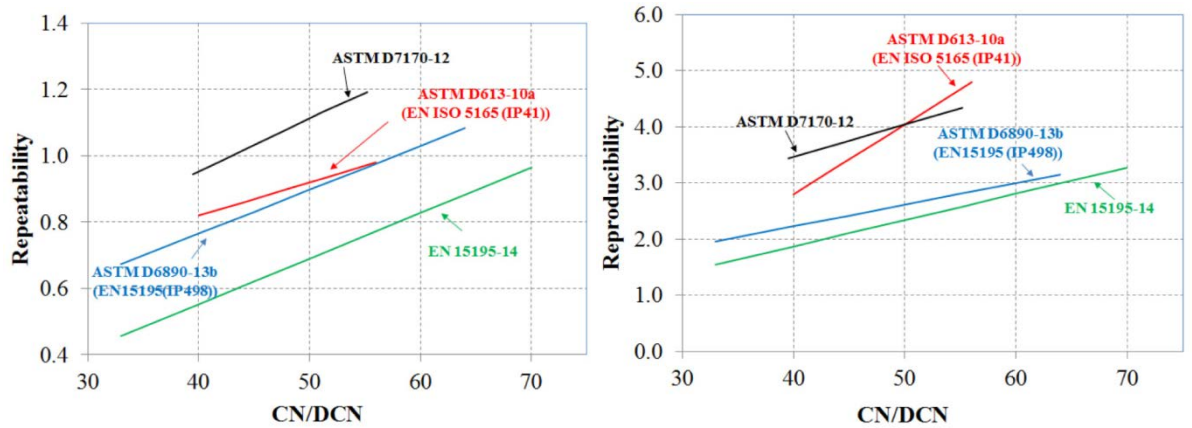
Methods employing an IQT and fuel ignition testing (FIT) utilize constant volume combustion apparatus to measure the ID time under a specific condition according to ASTM standards D6890 and D7170, respectively. A small amount of specimen fuel is injected into a constant volume combustion chamber with a controlled temperature and pressure environment, as stipulated by the ASTM standards. After each injection, a pressure curve is recorded, from which the ID can be measured. In these tests, the ID time is defined as the period between the SOI, when the injector needle starts to lift and the SOC, when 10% maximum pressure in the tested pressure curve is achieved. The measured ID time can be used to calculate the derived cetane number (DCN) according to ASTM D6890: <sup>[51]</sup>

$$DCN = 4.460 + \frac{186.6}{ID} \quad (2.2)$$

for  $3.1 \text{ ms} \leq ID \leq 6.5 \text{ ms}$ , or

$$DCN = 83.99 \cdot (ID - 1.512)^{-0.658} + 3.547 \quad (2.3)$$

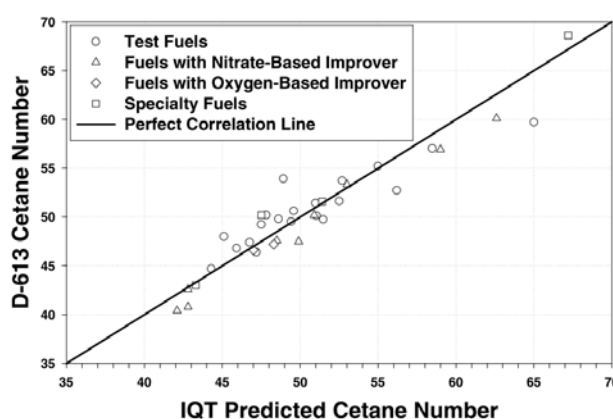
for  $ID < 3.1 \text{ ms}$  or  $ID > 6.5 \text{ ms}$ . The measurement should be repeated several times and the average calculated for the final result.



**Figure 2-5 Results of repeatability and reproducibility tests performed at the ASTM and the Energy Institute (EI) for different CN/DCN methods <sup>[52]</sup>**



**Figure 2-5** shows the precision of different CN measurement methods. The repeatability is defined as the maximum measurement difference obtained with identical samples by the same operator with one engine. Reproducibility is defined as the maximum measurement difference obtained with identical samples by different operators with different equipment. It can be seen that the IQT method (D6890) has a larger scaling range than for the CFR engine (D613) and FIT (D7170). Both the repeatability and reproducibility increase with CN. Furthermore, the IQT method has similar repeatability but much lower reproducibility compared with the CFR engine, especially at high CN.



**Figure 2-6 Comparison of DCN (IQT) and CN (CFR) based on 35 North American and European fuel tests** <sup>[53]</sup>

**Figure 2-6** shows a comparison of DCN and CN from testing various fuels, i.e., 31 fuels representative of commercially available Diesel fuels from North American and European sources and 4 research or specialty fuels. The results confirm that the DCN can be used to predict the CN of fuels (standard error of prediction 1.84).

A NIR analyzer can also be applied to measure the CN by detecting the absorption spectrum of the target fuel according to ASTM D6122. This is an efficient method for predicting the CN as about 10 - 15 measurements can be made in only a couple of minutes.

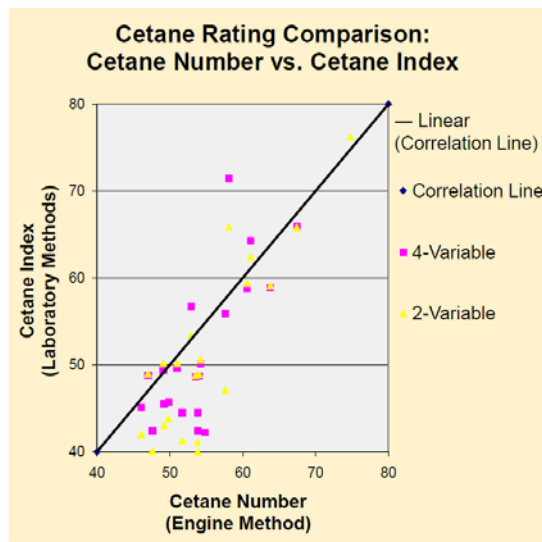
The CI can be calculated from numerous equations to predict CN on the basis of fuel density and distillation factor, avoiding the time and expense of conducting an experiment. Based on ASTM D976 standard, CI can be calculated using the following two-variable equation: <sup>[54]</sup>

$$CI_2 = 454.74 - 1641.416 \cdot \rho + 774.74 \cdot \rho^2 - 0.554 \cdot T_{50} + 97.803 \log^2(T_{50}) \quad (2.4)$$

Where  $\rho$  is the sample fuel density in g/L at 15 °C and  $T_{50}$  is the temperature at which 50 v/v of the sample has evaporated (in °C). A four-variable equation following the ASTM D975 standard to predict Diesel fuel grade 2-D S500 has also been developed: <sup>[55]</sup>

$$CI_4 = 45.2 + 0.0892 \cdot (T_{10} - 215) + (0.131 + 0.901 \cdot B_N)(T_{50} - 260) + (0.0523 - 0.42 \cdot B_N)(T_{90} - 310) + 0.00049 \cdot [(T_{10} - 215)^2 - (T_{90} - 310)^2] + 107 \cdot B_N + 60 \cdot B_N^2 \quad (2.5)$$

Where  $B_N = e^{-3.5(d-0.85)} - 1$  and  $T_{10}$ ,  $T_{50}$  and  $T_{90}$  are the 10, 50 and 90 vol.% sample fuel evaporated temperatures in °C.



*Figure 2-7 Comparison of cetane index and cetane number (CFR) <sup>[56]</sup>*

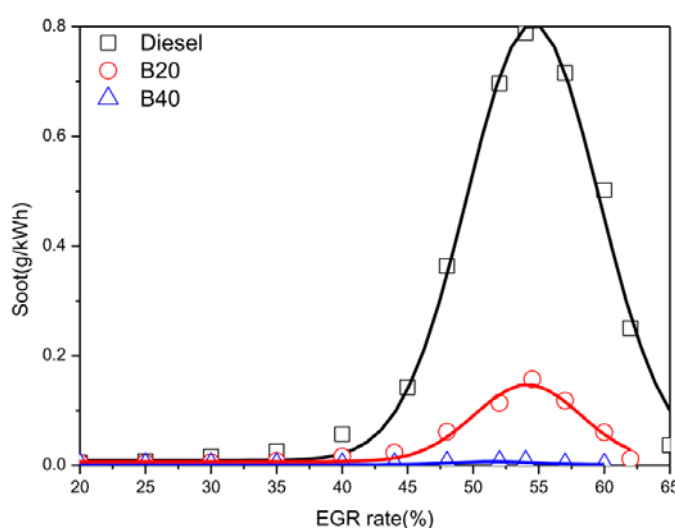
**Figure 2-7** shows a comparison of CI and CN. Although CI less closely follows CN than DCN, it is still possible to use CI to predict a rough trend for CN. Moreover, it can be seen that the 4-variable equation is more accurate than the 2-variable equation when the CN is below 55.

## 2.5 Effect of alcohol/Diesel blends on emissions

The oxygen content and other properties of alcohols have an important influence on emissions during combustion. Zhao et al. <sup>[57]</sup> reported that by promoting the proportion of premixed combustion phase, a longer ID time could be responsible for most of the soot reduction associated with alcohol blends. In addition, fuel-bound oxygen in alcohols could play a key role in oxidizing soot precursors in fuel-rich core regions of the fuel spray. Rakopoulos et al. <sup>[24,58]</sup> have reported similar results. The combustion of butanol/Diesel blends is generally slightly ‘leaner’ overall than that of Diesel and is assisted by the fuel-bound oxygen in butanol,

especially in fuel-rich regions of the burning spray. Sukjit et al. <sup>[59]</sup> have suggested that fuel properties such as viscosity, boiling and melting point affect spray properties and the C/H ratio may influence particulate matter formation. Valentino et al. <sup>[60]</sup> reported a longer flame lift-off length for butanol/Diesel blends than Diesel under the same operating conditions, which allows more space and time for air entrainment upstream of the spray. This leads to a better air fuel mixture, reducing the equivalence ratio in the combustion region, and thereby suppressing soot formation and promoting soot oxidation. <sup>[61]</sup>

Zhang et al. <sup>[62]</sup> showed that use of high EGR plus oxygenated additive (butanol) is an effective method to reduce soot and NO<sub>x</sub> emissions, as shown in **Figure 2-8**. As the EGR rate was increased, a peak in soot formation occurred at 45 – 65% EGR rate. There are three main reasons why the presence of butanol in the fuel can help to efficiently reduce soot formation. Firstly, its longer ID results in a more thoroughly premixed mixture, which suppresses soot formation. Secondly, oxygen atoms in the fuel are able to consume soot precursors by producing hydroxyl radicals, especially in the fuel rich regions. Thirdly, the lower viscosity and boiling temperature of *n*-butanol enhance the mixing process. Yao et al. <sup>[63]</sup> investigated the effect of using *n*-butanol and pilot and post injection on engine performance and emissions in a HD Diesel engine. Both multi-injection and the use of a butanol/Diesel blend were shown to be effective for reducing soot emissions. However, their individual impact on soot reduction was weakened when both were used together.



**Figure 2-8 Effects of fuel properties and EGR rate on soot emissions**

Butanol/Diesel blends also tend to show overall ‘leaner’ combustion and lower combustion temperatures than those achieved with pure Diesel. Butanol’s lower calorific value and higher heat of evaporation tend to override the effects of increased local oxygen concentration and

enhanced premixed combustion. <sup>[37,64]</sup> Consequently, NO<sub>x</sub> emissions from engines using Diesel/butanol blends are usually slightly lower than those achieved with pure Diesel. However Valentino et al. <sup>[65]</sup> reported that NO<sub>x</sub> emissions increase by 20% or 40% for n-butanol-Diesel blends compared with Diesel fuel in a four-cylinder LD duty Diesel engine. The different behaviour of NO<sub>x</sub> emissions when adding butanol in Diesel fuel may be related to the combustion mode used. By switching conventional combustion to PPC or LTC, soot and NO<sub>x</sub> emissions can be reduced simultaneously. PPC and LTC can be achieved, when the CN of the blend is low with introducing EGR, lowering the injection pressure such that the ID becomes longer than the injection duration. The switch observed with butanol/Diesel blends from producing more NO<sub>x</sub> to less NO<sub>x</sub> than Diesel fuel is demonstrated in ref [66], which shows the effect of changing the injection pressure and EGR level during the tests.

## 3 Experimental apparatus and methodology

### 3.1 Tested fuels

Diesel fuel, *n*-butanol, isobutanol, 2-ethylhexanol and *n*-octanol were used as the main components in the fuel mixtures. HVO and DTBP were added to the mixtures as CN improvers to compensate for the low CN of alcohols. The Diesel fuel used was a winter-type fuel produced by Statoil, meeting the EN590 standard but containing no biofuel (FAME). The Diesel fuel was used as the reference fuel in this study. Longer carbon chain alcohols, such as the butanol and octanol isomers, have a higher CN, LHV, flash point and density, lower vaporization latent heat and better lubricity and solubility in Diesel fuel than methanol and ethanol (shorter carbon chain alcohols), see **Table 2-1**. These properties of larger molecule alcohols are closer to those of Diesel fuel, making them easier to blend with Diesel. The tested alcohols were supplied by Perstorp AB in Sweden. HVO is a high CN biofuel. Therefore, it can be added to Diesel/alcohol blends to adjust their CN to a value similar to that of Diesel. The HVO used in this work was produced by Neste. DTBP is a widely used ignition improver that increases a blend's CN even when added in very small volumes <sup>[67]</sup>. The DTBP used in the project was called Trigonox B, produced by Akzo Nobel.

The CN of the different blends was determined using a CFR engine complying with the ASTM D-613 standard. The CN values of the blends used in this work are shown in **Table 3-1** (superscript L denotes that the blends were tested in a single-cylinder LD engine, H stands for a single-cylinder HD engine and ML stands for a multi-cylinder engine).

To match the CN of Diesel (52), various amounts of DTBP or HVO were added to the alcohol/Diesel blends. The blends were named systematically as follows: the first part denoted the alcohol used (isoBu = isobutanol, nBu = *n*-butanol, 2EH=2-ethylhexanol and nOc = *n*-octanol), the second part (numbers) denoted the proportion of alcohol in the blend (i.e. 10, 20, or 30 for 10%, 20%, and 30%, respectively) and the last letter denoted the additive used (H for HVO, D for DTBP).

Butanol isomers and HVO have poorer lubricity than specified by EN590. Therefore, 200 ppm (parts per million) by weight of a lubricity additive, PC32, was added to the blends containing butanol isomers or HVO.

In this project, blends with 10 and 20 vol.% butanol isomers were selected for two main reasons. Firstly, the blends' high percentage of butanol was expected to have a strong influence on the combustion characteristics and emissions. When butanol isomers are mixed in Diesel at levels

higher than 30 vol.%, NO<sub>x</sub> emissions and fuel consumption have been shown to increase, whereas the maximum brake power and maximum torque may decrease.<sup>[68]</sup> Secondly, as can be seen from the data in **Table 3-1**, the effect of DTBP in increasing the CN seems to be close to its limit for the blends nBu20D and isoBu20D, and therefore it may not have been possible to raise the CN of a blend with 30% isobutanol to ~52. Therefore, the selected blends were seen as a good compromise.

**Table 3-1 CN of the tested fuels**

Blends	Diesel vol. %	<i>n</i> -Butanol vol. %	Isobutanol vol. %	2-Ethylhexanol vol. %	<i>n</i> -Octanol HVO vol. %	DTBP mg/kg	CN -
Diesel <sup>L,H,ML</sup>	100	-	-	-	-	-	52
nBu10H <sup>L,H</sup>	70	10	-	-	20	-	50.6
nBu20H <sup>L,H,ML</sup>	40	20	-	-	40	-	50.3
nBu10D <sup>L,H</sup>	90	10	-	-	-	600	51.3
nBu20D <sup>L,H</sup>	80	20	-	-	-	12000	~49.0
isoBu10H <sup>H</sup>	60	-	10	-	30	-	51.7
isoBu20H <sup>L,H</sup>	20	-	20	-	60	-	52.5
isoBu20D <sup>L,H</sup>	80	-	20	-	-	12000	49.0
2EH30D <sup>L,H</sup>	70	-	-	30	-	6000	49.9
2EH30H <sup>L,ML</sup>	30	-	-	30	40	-	51.3
nOc30H <sup>L</sup>	50	-	-	-	30	20	53.1
nOc30D <sup>L</sup>	70	-	-	-	30	800	50.8

<sup>L</sup> denotes LD engine tests, <sup>H</sup> denotes HD engine tests, <sup>ML</sup> denotes multi-cylinder LD engine tests.

**Table 3-2** show the properties of the fuels tested in the cold start experiments. The blends showed a lower cloud point and cold filter plugging point than Diesel fuel, which are both beneficial for engine cold starts.

**Table 3-2 Cold start properties of fuels**

Properties	Unit	Diesel	Bu20H	2EH30H
Viscosity @ 40 °C	mm <sup>2</sup> /s	3.037	2.444	3.033
Cloud point	°C	-9	-16	-18
Cold filter plugging point	°C	-25	-35	-36
Flash point	°C	82	38	73
C:H:O	-	12:23:-	25:53:1	26:54:1

## 3.2 Tested engines

To investigate the effects of using alcohols in Diesel fuel, three types of engines were used. A single cylinder LD engine and a single cylinder HD engine were utilized to study the effect of using Diesel and alcohol/Diesel blends on performance and emissions. In addition, a four-

cylinder LD engine was applied to study the cold start behaviour when using alcohol/Diesel blends.

### 3.2.1 HD engine specifications and conditions

A 2 litre AVL 501 single cylinder HD Diesel engine was employed, which was equipped with a common rail injection system and a cylinder head and piston based on the Volvo Powertrain D12C engine. **Table 3-3** shows the engine's specifications. The test engine used a Delphi F2 distributed pump Diesel common rail system, which enabled the use of higher (up to 270 MPa) and more stable injection pressures.

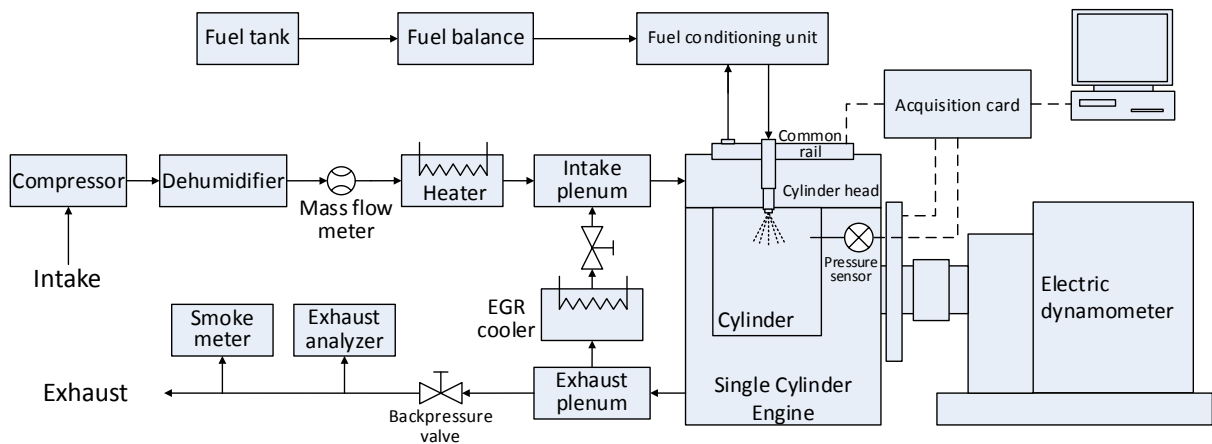
**Table 3-3 Specifications of the single-cylinder HD engine**

Engine type	AVL 501 Single cylinder
Bore	131 mm
Stroke	150 mm
Valves	4
Connecting rod length	260 mm
Compression ratio	17:1
Fuel injection system	Common rail
Injection pressure	180 MPa
Nozzle	5 holes

**Figure 3-1** shows a schematic of the HD engine test bed. Before the fuel balance, the fuel tank was mounted on a digital balance so that the instantaneous weight of the remaining fuel could be monitored from the control room. An AVL 733S fuel balance was used to measure the fuel mass flow rate, and the fuel was passed through a conditioning unit before delivery to the pumping injector. A Kistler 7061B pressure sensor, a Kistler 3066A01 piezo amplifier and an Osiris data acquisition system were used to acquire cylinder pressure data at 0.1 crank angle degrees (CAD) resolution for 100 cycles. The EGR was adjusted by controlling the backpressure with a valve placed in the exhaust pipe. The recirculated exhaust gases were cooled by a water cooler before being mixed with the compressed intake air, whose humidity and temperature were controlled.

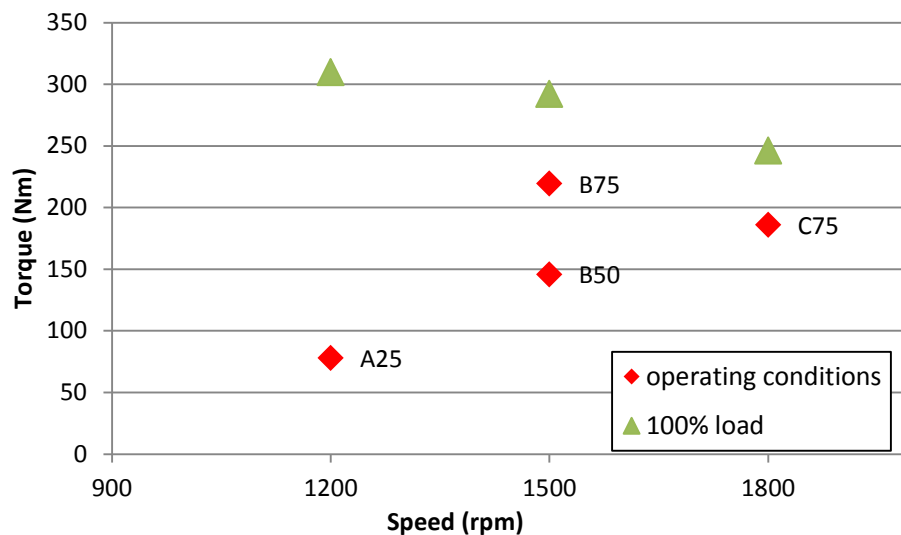
The concentrations of HC, nitric oxide (NO), carbon monoxide (CO), CO<sub>2</sub> and oxygen (O<sub>2</sub>) in ppm (by volume) in the exhaust gases were measured using an AVL AMA i60 exhaust measuring system. HC in exhaust gases was measured using the i60 flame ionization detector (FID) with heated sampling line. The i60 FID had a reproducibility of 0.5% of the full scale. NO was measured by the i60 chemiluminescence detector (CLD) with heated sample line and super low quenching. The i60 CLD had a reproducibility of 0.5% of the full scale. CO<sub>2</sub> and CO

were measured by the i60 infrared detector (IRD), which had a reproducibility of 0.5% of the full scale. To detect CO<sub>2</sub> and CO, the sample gas had to be first cooled down so that water condensed out. Soot emission measurements were performed using an AVL 415 smoke meter. The filter smoke number (FSN) was measured based on the blackening of filter paper through which raw exhaust gas was passed.



**Figure 3-1 Schematic of the HD engine experimental setup**

**Figure 3-2** shows the operating conditions of the HD Diesel engine. Four operating points from the European Stationary Cycle were chosen: A25, B50, C75 and B75. B50 was chosen as the reference point.



**Figure 3-2 Operating conditions of the HD engine**



To investigate the scope for using butanol/Diesel blends in Diesel engines, all of the tested engine settings (see **Table 3-4**) were based on factory calibration data for the Volvo Powertrain D12C production engine. All the blends were tested using identical engine settings.

**Table 3-4 Operating conditions used in the HD engine tests**

Operating conditions	Unit	A25	B50	C75	B75
Torque	Nm	78.0	145.9	186.0	219.5
Speed	Rpm	1200	1500	1800	1500
Injection pressure	MPa	180	180	180	180
Injection duration	$\mu$ s	660	1000	1300	1400
Start of injection	CAD BTDC	4.52	7.80	4.50	9.40
EGR	%	29.0	25.9	21.9	24.1
Boost	Mbar	256	940	1735	1464

A common rail injection system was applied in this study instead of the usual electronically controlled unit. Therefore, the injection duration, injection pressure and SOI were adjusted to match the production engine settings as closely as possible. The EGR rates used in this work were 20% to 100% greater than those of the production engine settings to maintain specific NO<sub>x</sub> emissions at 1.8 g/kWh when using pure Diesel, which is just below the 2.0 g/kWh Euro V limit. The same EGR rates were used for all blends, as shown in **Table 3-4**.

### 3.2.2 LD engine specifications and conditions

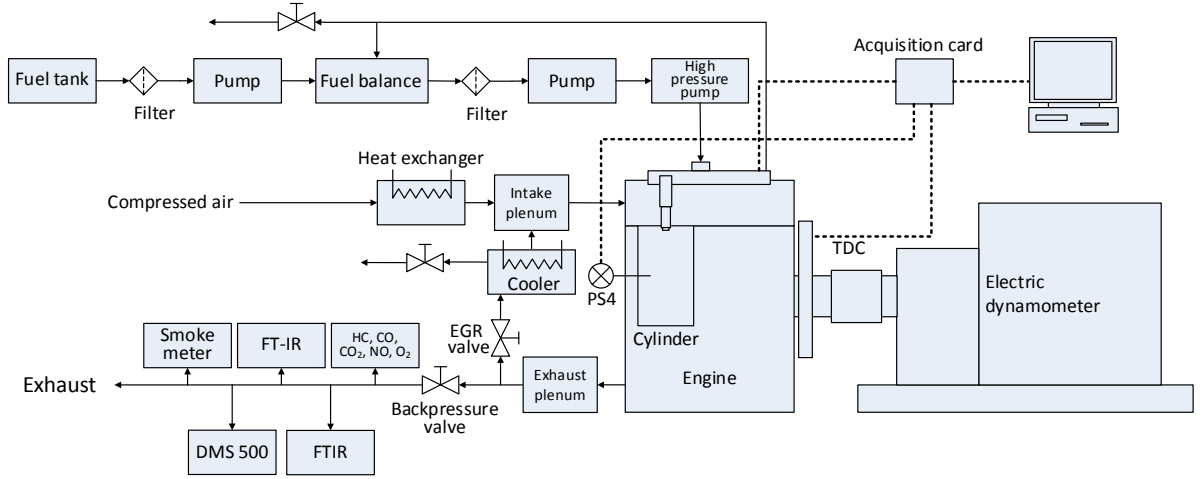
Single cylinder LD engine tests were conducted in a Ricardo hydra engine equipped with a Volvo NED4 cylinder head and a common rail injection system. **Table 3-5** shows the engine's specifications.

**Table 3-5 Specifications of the single-cylinder LD engine**

Engine type	Ricardo Hydra engine
Bore	82 mm
Stroke	93 mm
Compression ratio	15.8:1
Fuel injection system	Common rail

**Figure 3-3** shows a schematic of the LD engine test bed. Fuel mass flow was measured by an AVL 730 fuel balance. A Denso injector was used to generate up to 4 pulse injections per cycle. An AVL GU12S-10 pressure transducer was installed to measure the in-cylinder pressure based on a charge difference. The change in signal was amplified by a Kistler 5011 piezo amplifier

and acquired by an Indi Com system. The crank angle resolution of the cylinder pressure was 0.2 CAD. A water cooled EGR system was used, which comprised a control valve (EGR valve in **Figure 3-3**) to adjust the EGR flow from the exhaust plenum to the intake plenum and an air operated valve (backpressure valve) to establish the backpressure of the exhaust plenum by adjusting the exhaust gas flow rate to the barometric environment.



**Figure 3-3 Schematic of the LD engine experimental setup**

A JUM model 3-300 flame ionization analyzer was used to measure HCs in the exhaust gases. The concentration of NO was measured using a Rosemount analytical process chemiluminescence NO/NO<sub>x</sub> analyzer (951A), which had a precision of 0.5% of full scale. The sampling line of exhaust gases was heated to 190 °C to avoid water condensation prior to being passed to the HC and NO analyzers.

After condensing water in the sample gas, CO and CO<sub>2</sub> were measured by a Rosemount Binos 1001/1004 with less than 2% accuracy. CO<sub>2</sub> was measured at both the intake and exhaust system to calculate the EGR ratio as follows:

$$EGR = \frac{CO_{2\text{ intake}} - CO_{2\text{ air}}}{CO_{2\text{ exhaust}} - CO_{2\text{ air}}} \times 100\% \quad (3.1)$$

Soot emission measurements were performed with an AVL 415 smoke meter, similar to the one used in the HD engine tests. PM size distributions were measured using a DMS500 fast particulate spectrometer based on the principle that particulates with different masses attach to different positions on the detector. The DMS500 system incorporated two stages of dilution to comply with the engine sampling environment. To maintain a good signal-to-noise ratio, the

second stage of dilution was adjusted when changing the operating conditions, but it was not adjusted when changing fuels. PM size distributions were measured by counting the number of particulates with a positive charge at different positions on the detector.

Based on the New European Driving Cycle, four different operating points were chosen for the LD engine tests, as shown in **Table 3-6**. All of the engine settings were based on factory calibration data for Volvo commercial engines, and all the blends were tested under the same engine settings. Because the dynamometer was run in fixed speed mode, the torque varied for the different fuels as a result of their different LHVs. A multi-injection strategy and EGR were applied in these tests. Swirl management was employed to adjust the swirl ratio to match the various engine loads.

**Table 3-6 Operating conditions used in the LD engine tests**

Operating conditions	1	2	3	4
Speed (rpm)	1200	1280	1810	2000
Torque (Nm)	5	30	23	36
Intake air pressure (bar, abs)	1.05	1.35	1.58	2.19
Pilot1 SOI (CAD BTDC)	12	7.0	17	16
Pilot2 SOI (CAD BTDC)	7	3.0	10.0	9.5
Main SOI (CAD BTDC)	1	-2.0	3	2
Post SOI (CAD BTDC)	-	-12.5	-9.5	-13.5
Injection pressure (MPa)	35	80	67	91
EGR (%)	37.9	19.4	27.3	22.5

Eleven of the fuels listed in **Table 3-1** were tested in the LD engine under the four selected operating conditions. Operating condition 2 was utilized as the reference point during the LD engine tests. For each fuel test, this reference point was performed prior to each change of operating condition to calculate error bars, and hence repeatability, of the results. After each blend test, the engine was run with Diesel fuel under reference operating condition to check that the engine's performance had not changed.

### **3.2.3 Multi-cylinder engine specifications and conditions**

A four cylinder Volvo Car's VED4 engine equipped with a high performance (HP) turbo system and common rail system was used for the cold start tests. **Table 3-7** shows the engine specifications. The tests were conducted in Volvo cold start engine test facilities with a set-up close to vehicle conditions. Prior to the tests, the engine was cooled to 2 °C below the target starting temperature. The temperature was then adjusted to the starting temperature and kept constant for 2 hours. The engine was cooled using the cooling equipment of the room and cooling fans directed at the engine.

**Table 3-7 Specifications of the multi-cylinder LD engine**

Engine type	VED4 HP
Bore	82 mm
Stroke	93.2 mm
Displacement	1.9691
Compression ratio	15.8:1
Fuel injection system	Common rail, 7 holes injector
Injection pressure	Approx. 45 MPa at start, 20-180 MPa during run
Firing order	1,3,4,2
Glow plug tip temp	1250 °C

After performing a cold start, data were collected for 120 seconds at idling. The engine was subsequently run at 2200 rpm until the cooling water temperature reached 80 °C. Afterwards, the engine was shut down and another cooling sequence was initiated. Three fuels were tested: Diesel fuel, nBu20H and 2EH30H (**Table 3-8** shows their properties). Each of the fuels was tested three times at each studied temperature, i.e. 0, -10, -20, -25 and -30 °C. The blends showed a lower cloud point and cold filter plugging point than Diesel fuel, both of which are beneficial for engine cold starts.

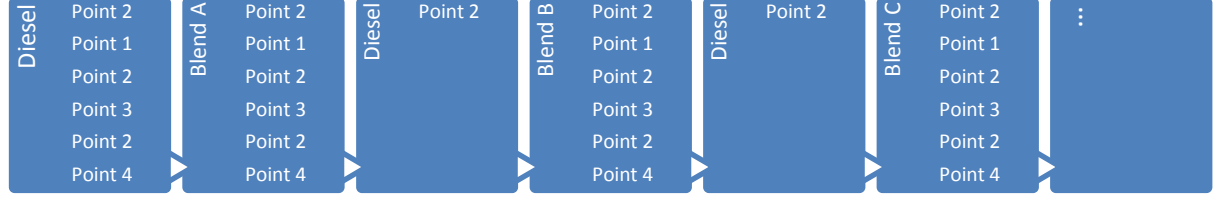
**Table 3-8 Properties of the fuels used in the cold start tests**

Properties	Unit	Diesel	Bu20H	2EH30H
Viscosity@40 °C	mm <sup>2</sup> /s	3.037	2.444	3.033
Cloud point	°C	-9	-16	-18
Cold filter plugging point	°C	-25	-35	-36
Flash point	°C	82	38	73

### 3.3 Measurement procedure

The experiments in both the LD and HD engines were initially conducted with Diesel fuel. During the tests, the operating conditions (except reference point - B50 for the HD engine and point 2 for the LD engine) were performed in sequence. Before changing the operating condition, the engine was run at the reference point to check the repeatability of the results. Next, the Diesel fuel was replaced by a blend fuel and the same procedure was repeated for each blend. Before each change of blend, the engine was run with Diesel fuel at the reference point. When changing from one fuel to another, the fuel balance was emptied and filled with the new fuel twice, after which the engine was operated for at least 30 min with the new fuel at the reference operating point to consume residual fuel in the fuel line before starting the

experimental runs with the new blend. **Figure 3-4** shows the testing procedure used in both the LD and HD engine tests.



**Figure 3-4 Testing procedure**

## 3.4 Measurement evaluation

### 3.4.1 Heat release rate

Heat release curves acquired during the HD engine tests were evaluated using an Osiris data acquisition system. Generally, the heat release rate was calculated using the first law of thermodynamics:

$$\delta Q_{ch} = dU + \delta Q_{ht} + \delta W \quad (3.2)$$

where  $U$  is the internal energy of the cylinder contents,  $Q_{ht}$  is the heat transfer to the chamber walls and  $W$  is the work done on the piston. If it is assumed that the contents of the cylinder can be modelled as an ideal gas,  $dU$  is given by

$$dU = \frac{c_v}{R} p dV + \frac{c_v}{R} V dp \quad (3.3)$$

where  $R$  is the ideal gas constant,  $p$  is the cylinder pressure and  $V$  is the volume of the combustion chamber.  $c_v$  is the specific heat capacity at constant volume, which can be calculated as below:

$$c_v = c_p - R \quad (3.4)$$

where  $c_p$  is the specific heat capacity at constant pressure and can be calculated by:

$$c_p = (a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4) \cdot R \quad (3.5)$$

The heat transfer between the cylinder contents and chamber wall can be defined as follows:

$$Q_{ht} = hA(T - T_w) \quad (3.6)$$

where  $h$  is the heat transfer coefficient,  $A$  is the exposed combustion chamber surface area,  $T$  is the temperature of the cylinder gas and  $T_w$  is the cylinder wall temperature. The Woschni heat transfer coefficient <sup>[69]</sup> can be expressed as

$$h = 3.26 \times B^{-0.2} \cdot p^{0.8} \cdot T^{-5.5} \cdot v^{0.8} \quad (3.7)$$

where  $B$  is the cylinder diameter,  $T$  is the cylinder pressure and  $v$  is the average cylinder gas velocity.

$\delta W$  can be calculated as below:

$$\delta W = p dV \quad (3.8)$$

### 3.4.2 Evaluation related to changing fuel

The LHV is an important property of a fuel because it influences the combustion behaviour and emissions. For a blend comprising Diesel fuel, alcohol and an ignition improver, LHV depends on the proportions of the individual components, as shown below:

$$LHV_{blend} = \sum_i^n V_i \cdot \rho_i \cdot LHV_i \quad (3.9)$$

where  $V_i$ ,  $\rho_i$  and  $LHV_i$  are the volume percentage, density and LHV of component  $i$ , respectively. For blends, Yao et al. <sup>[63]</sup> have suggested a correction for the fuel consumption based on the Diesel equivalent mass value of blends with a LHV than Diesel fuel:

$$m_{correct} = m_{fuel} \cdot \frac{\frac{\sum_i^n V_i \cdot \rho_i \cdot LHV_i}{\sum_i^n V_i \cdot \rho_i}}{LHV_{diesel}} \quad (3.10)$$

where  $m_{fuel}$  is the actual measured fuel consumption.

When changing Diesel fuel to blends, the different hydrogen, nitrogen and oxygen content and density of HC will influence the specific emissions. Therefore, factors in equations need to be determined for specific emissions.

Gas emissions from exhaust gases are normally measured in parts per million (ppm) by volume (soot emissions are converted to mg/kg). To make emissions data more comparable, they need

to be converted to specific values. Specific emissions of soot, HC, CO<sub>2</sub>, CO and NO<sub>x</sub>, can be derived according to the following equation:

$$e = \frac{q_c \times 3.6}{P} \quad (3.11)$$

Where  $q_c$  is the emission component mass flow rate in mg/s and  $P$  is the power in kW. The soot mass flow rate in the exhaust can be calculated as below:

$$q_{Soot} = \frac{1}{0.405} \times 4.95 \cdot FSN \cdot e^{0.38 \times FSN} \times \frac{1}{1.169} \cdot (q_{mf} + q_{mair}) \quad (3.12)$$

For HCs, CO<sub>2</sub>, CO and NO<sub>x</sub>, the emission component mass flow rate is

$$q_c = \frac{\rho_c}{\rho_e} \cdot c \cdot (q_{mf} + q_{mair}) \quad (3.13)$$

Where  $\rho_c$  is the density of one exhaust gas component in kg/m<sup>3</sup>,  $\rho_e$  is the density of the exhaust gas in kg/m<sup>3</sup>,  $c$  is the one component concentration in ppm,  $q_c$  is the emission component mass flow rate in mg/s,  $q_{mf}$  is the instantaneous fuel mass flow rate in kg/s and  $q_{mair}$  is the instantaneous dry intake air mass flow rate in kg/s.

In addition, the density of the exhaust gas can be derived as follows <sup>[70, 71]</sup>:

$$\rho_e = \frac{1000 + H_a + 1000 \times \frac{q_{mf}}{q_{mair}}}{773.4 + 1.2442 \times H_a + k_f \times 1000 \times \frac{q_{mf}}{q_{mair}}} \quad (3.14)$$

with

$$k_f = 0.05594 \cdot w_{ALF} + 0.0080021 \cdot w_{DEL} + 0.0070046 \cdot w_{EPS} \quad (3.15)$$

where  $H_a$  is the intake air humidity (g water per kg dry air) and  $w_{ALF}$ ,  $w_{DEL}$  and  $w_{EPS}$  are the hydrogen, nitrogen and oxygen content of the fuel (in wt.%), respectively.

As mentioned above, CO<sub>2</sub> and CO were measured as dry gas. Therefore, a dry-to-wet correction factor was needed to convert the measured value to a real (wet) value according to the following equation:

$$c_w = k_w \cdot c_d \quad (3.16)$$

where  $c_d$  is the dry gas concentration in ppm and  $k_w$  is the dry-to-wet correction factor. Under the experimental conditions used in this study, the dry-to-wet correction factor was calculated as follows:

$$k_w = \left(1 - \frac{1.2442 \times H_a + 111.19 \times w_{ALF} \times \frac{q_{mf}}{q_{mair}}}{773.4 + 1.2442 \times H_a + \frac{q_{mf}}{q_{mair}} \times k_f \times 1000}\right) \times 1.008 \quad (3.17)$$

The  $NO_x$  emission concentration also needed to be corrected using the following equation:

$$c_{corr} = \frac{1}{1 - 0.0182 \cdot (H_a - 10.71) + 0.0045 \cdot (T_{air} - 25)} \cdot c_{NOx} \quad (3.18)$$

where  $T_{air}$  is the intake air temperature and  $c_{NOx}$  is the measured concentration of  $NO_x$  in ppm.

### 3.4.3 Statistical analysis

Statistical data analysis methods were used to compare the performance and exhaust emissions of the different engines when fuelled with alcohol/Diesel blends and Diesel fuel. In total, 12 different fuels were used in the tests: 11 fuels in the LD tests and 9 fuels in the HD tests. In addition, the effects of two types of engines and four load points for each engine were considered, suggesting 3 test variables in total.

Since the results were evaluated for different operating conditions and two engine concepts, normalized data were employed in the data analysis: absolute values obtained with different fuels under the same conditions were divided by the corresponding Diesel value. This enabled data for the two different types of engine to be compared. Analysis of variance (ANOVA) tables were used to check the significance of the variables on engine combustion behaviour and emissions. Differences were analyzed between the types of engine, CN improver and individual fuels used. The confidence interval was set to 95%.

Two methods were used to check the repeatability of the results and stability of combustion. Error bars represented the standard deviation of repeated reference measurements made between each change of operating conditions. Thus, the error bars showed the repeatability of the results for a particular fuel and operating condition. In addition, the coefficient of variation (COV) of the IMEP was used to show the cycle-to-cycle variation, as calculated below:



$$COV_{IMEP} = \frac{\sqrt{\frac{1}{n} \sum_i^n (IMEP_i - \overline{IMEP})^2}}{\overline{IMEP}} \times 100\% \quad (3.19)$$

where  $IMEP_i$  is the IMEP of individual cycle and  $\overline{IMEP}$  is the mean value of IMEP in one measurement.



## 4 Results

### 4.1 Summary of Paper I

The results of the Paper I can be divided into two main parts – engine performance and exhaust emissions.

With the same CN number as Diesel, all the tested fuels (alcohol/Diesel blends and Diesel fuel) showed a similar SOC and heat release process, regardless of which additive (HVO or DTBP) was used in the blends. The similar ID time and heat release curve profiles indicate that all the fuels generated a similar level of premixed combustion. All of the tested fuels exhibited similar peak cylinder pressures and locations of maximum pressure. In addition, under most operating conditions, the maximum pressure for pure Diesel fuel was slightly lower than that of the blends, indicating that the combustion of the blends was more intense than that of Diesel fuel. The presence of alcohol in the blends is likely accelerate the combustion speed, especially of diffusion combustion. All the fuels examined in this work showed low cycle-to-cycle variation, with COV values of less than 3%. Under most operating conditions, the COV for pure Diesel fuel was higher than that for the blends, suggesting that the combustion of the blends was slightly more stable than that of Diesel fuel.

Soot emissions clearly decreased with increasing fuel oxygen content. Oxygen atoms in the alcohol components of the blends have been suggested to suppress soot formation by reducing the concentration of soot precursors <sup>[72]</sup>. The longer flame lift-off length obtained with blends leads to greater air entrainment, thus reducing soot formation. In the present study, CO emissions followed the same trend as for soot emissions, i.e. decreasing as the alcohol content of the fuel was increased. Combustion of the blends produced higher NO<sub>x</sub> emissions than those from pure Diesel. The increased NO<sub>x</sub> emissions of the blends compared to Diesel seemed to correlate with the oxygen content in the fuel. The formation of NO<sub>x</sub> emissions is governed by the equivalence ratio and temperature of combustion. Owing to the blends' higher oxygen content, their combustion is likely to produce a slightly higher local oxygen concentration than achieved with Diesel. Blends also tend to generate a slightly higher peak pressure than Diesel, causing a slightly higher peak temperature and increased NO<sub>x</sub> emissions. Use of alcohol/Diesel blends also slightly increased HC emissions. The differences in HC emissions between the different fuels were most pronounced at low load.

## 4.2 Summary of Paper II

A comparison between the HD engine results and LD engine results was investigated in Paper II.

Like the results in the HD engine, alcohol/Diesel blends advanced the CA50 and CA90 compared with Diesel fuel in the LD engine. The presence of alcohol in Diesel fuel influenced the duration of premixed and diffusion combustion. This was likely due to a charge-cooling effect, which opposes the effects of better atomization and evaporation. As a result of these conflicting factors, the combustion duration can be either extended or shortened. Moreover, butanol isomers and octanol isomers have higher laminar burning velocities than Diesel, which promotes the combustion and reduces the combustion duration for the tested blends.

The ITE increased when using blends at the medium and high load operating conditions compared with Diesel. This can be explained by the shorter combustion duration obtained with the blends compared with Diesel fuel. In addition, the alcohol/Diesel blends promoted complete combustion, improving the thermal efficiency.

Soot emissions clearly decreased with increasing fuel oxygen content in the fuel. The average soot reductions obtained when changing from no oxygen in the fuel (pure Diesel) to 4.3% oxygen content (for around 20% butanol in Diesel) were in the range 44.7% to 83.7% for blends with the two different CN improver additives and engines. This suggests that a dramatic reduction in soot emissions can be achieved by using blends instead of Diesel fuel. Fuel-borne oxygen have the dominant influence in soot reduction in this conventional combustion. In the present study, the HVO-containing blends showed greater soot reduction (51.1% and 83.7%) than the DTBP-containing blends (44.7% and 74.8%). This can be explained by the partial replacement of fossil Diesel fuel by aromatic-free HVO. Overall, the HD engine showed a greater reduction in soot emissions in the tests than the LD engine.

The alcohol/Diesel blends produced more NO emissions (9.9%) than Diesel fuel. This may be because the alcohol/Diesel blends generated a slightly higher local temperature, which promotes NO formation. Moreover, in the HD engine, the difference in average NO emissions between the DTBP-containing blends (14.6% increase compared with Diesel) and HVO-containing blends (10.4%) was statistically significant. This is most likely due to the different properties of Diesel fuel and HVO, and the effect of addition of DTBP.

At temperatures of 0 and -10 °C, all the tested fuels showed comparable start and idling stability. At temperatures of -20, -25 and -30 °C, the nBu20H fuel showed slightly improved idling stability compared to the other fuels.

## 5 Conclusions

In this study, the effects of alcohol (*n*-butanol, isobutanol, *n*-octanol and 2-ethylhexanol) Diesel blends on engine performance and emissions were investigated in both a single-cylinder LD engine and a single-cylinder HD engine with production engine settings. In order to use an unmodified engine, different amounts of HVO and DTBP were added to the blends to adjust their CN to that of Diesel fuel (CN of 52).

The tested alcohol/Diesel blends with CN improver showed very similar engine performance, such as coincident SOC and heat release profile. All of the tested fuels provided similar gross indicated thermal efficiencies. Further, the blends showed slightly higher indicated thermal efficiencies than Diesel fuel at medium and high load. The higher indicated thermal efficiency was attributed to the faster rate of burning of the blends than Diesel fuel, especially in diffusion controlled combustion. The cycle-to-cycle variation of the tested blends was lower than that of Diesel.

The soot emissions produced from tested alcohol/Diesel blends were much lower than those from Diesel fuel for both engines. The oxygen content of the fuels was shown to play a key role in reducing soot emissions. In particular, soot emissions declined sharply as the oxygen mass fraction of the fuel increased. Further, replacing some fossil Diesel with HVO as a CN improver in the blends significantly reduced soot emissions. Alcohol/Diesel blends yielded higher NO emissions than pure Diesel. In addition, less NO was produced from the HVO-containing blends than the DTBP-containing blends.

In the single-cylinder HD engine, blending alcohol and Diesel reduced CO emissions relative to those achieved with pure Diesel, but all the tested fuels yielded similar HC emissions.

In the single-cylinder LD engine, the total PM number was reduced when using alcohol/Diesel blends and the PM diameter showed a tendency to decrease with increasing oxygen fraction in the fuel.

In the four-cylinder LD engine cold start tests, nBu20H and 2EH30H not only fulfilled the EN590 winter fuel standard but also could be ignited normally down to -30 °C.

In conclusion, our results show that from a combustion point of view, it is possible to use renewable fuels, such as *n*-butanol, isobutanol, *n*-octanol or 2-ethylhexanol, mixed with Diesel and ignition improver in existing Diesel engines without the need for engine modifications.



## 6 Future work

Future work in this project will attempt to use alcohol/Diesel blends without any CN improver to achieve PPCI. In this new combustion mode, reduced fuel consumption and a relatively high gross indicated thermal efficiency are expected.

As mentioned in the previous chapter, the use of alcohol/Diesel blends in Diesel engines is able to achieve PPC owing to their low CN, which means that multi-injection or high EGR level will not be necessary in the experiments. PPC will be performed in both a single-cylinder HD engine and a single-cylinder LD engine. Butanol and octanol isomers will likely need to be mixed with Diesel fuel to lower the CN of the blends. The combustion performance and exhaust gases emissions, such as HC, CO, NO<sub>x</sub> and soot, will be investigated.

To gain a better understanding of conventional combustion and PPC with alcohol/Diesel blends, it would be useful to investigate the breakup and evaporation of the fuel jet in the constant volume spray chamber. Thus, the blends will be tested under various conditions. Since the spray formation affects the temperature field distribution and extent of fuel air mixing, it is important to study the fundamental spray characteristics to explain the combustion behaviour in internal combustion engines.





## Abbreviations

<b>BTDC</b>	before top dead center	<b>ID</b>	ignition delay
<b>BTL</b>	biomass to liquid	<b>IMEP</b>	indicated mean effective pressure
<b>CAD</b>	crank angle degrees	<b>IQT</b>	ignition quality tester
<b>CFR</b>	co-operative fuel research	<b>IRD</b>	infrared detector
<b>CI</b>	cetane index	<b>ITE</b>	indicated thermal efficiency
<b>CLD</b>	chemiluminescence detector	<b>LD</b>	light duty
<b>CN</b>	cetane number	<b>LTC</b>	low temperature combustion
<b>COV</b>	coefficient of variation	<b>NIR</b>	near infra-red
<b>DCN</b>	derived cetane number	<b>NO<sub>x</sub></b>	nitrogen oxides
<b>DTBP</b>	di-tertiary-butyl peroxide	<b>PPC</b>	partially premixed combustion
<b>EGR</b>	exhaust gas recirculation	<b>ppm</b>	parts per million
<b>FID</b>	flame ionization detector	<b>Rpm</b>	revolutions per minute
<b>FIT</b>	fuel ignition testing	<b>SOC</b>	start of combustion
<b>FSN</b>	filter smoke number	<b>SOI</b>	start of injection
<b>GHG</b>	greenhouse gas	<b>TDC</b>	top dead center
<b>HC</b>	hydrocarbon	<b>Vol.</b>	Volume
<b>HCCI</b>	homogeneous charge compression ignition	<b>Wt.</b>	weight
<b>HD</b>	heavy duty	<b>WTW</b>	well to wheels
<b>HVO</b>	hydrotreated vegetable oil		



## References

1. Eurostat, “Greenhouse Gas Emissions by Sector (Source: EEA),” Code: tsdcc210, <http://ec.europa.eu/eurostat/tgm/table.do?tab=table&plugin=1&language=en&pcode=tsdcc210>.
2. Environmental Protection Agency Inventory of U.S. “Greenhouse Gas Emissions and Sinks: 1990 – 2013,” 2015.
3. BP Distribution Services, “BP Statistical Review of World Energy June 2015,” <http://bp.com/statisticalreview>, accessed Nov. 2015.
4. Commission Staff Working Paper, “Analysis of Options Beyond 20% GHG Emission Reductions: Member State Results,” 2012.
5. European Council 23/24 October 2014 – Conclusions, 2014.
6. Swedish Institute, “Energy: Generating Power for a Sustainable Future,” 2015.
7. Pires and R. Schechtman, “International Biofuels Policies,” Ethanol and Bioelectricity: Sugarcane in the Future of the Energy Matrix, 2010.
8. R. Gray and B. Evans, “Biofuels Annual Canada Biofuels Annual 2013,” 2013.
9. European Commission, “Europe’s Energy Position: Markets and Supply – Market Observatory for Energy,” 2009.
10. European Expert Group, “Future Transport Fuels,” 2011.
11. Demirbas, “Biofuels Sources, Biofuel Policy, Biofuel Economy and Global Biofuel Projections,” *Energy Convers. Manag.*, 49,(8):2106–2116, 2008.
12. H. Aatola, M. Larimi, and T. Sarjovaara. “Hydrotreated Vegetable Oil (HVO) as a Renewable Diesel Fuel: Trade-off between NOx, Particulate Emission, and Fuel Consumption of a Heavy Duty Engine.” SAE Paper, 2008-01-2500.
13. K. Sugiyama, I. Goto, K. Kitano, and K. Mogi, “Effects of Hydrotreated Vegetable Oil (HVO) as Renewable Diesel Fuel on Combustion and Exhaust Emissions in Diesel Engine,” *SAE Int. J. Fuels Lubr.*, 5(1):205–217, 2012.
14. M. Ni, D. Y. C. Leung, and M. K. H. Leung, “A Review on Reforming Bio-Ethanol for Hydrogen Production,” *Int. J. Hydrogen Energy*, 32(15):3238–3247, 2007.
15. C. Jin, M. Yao, H. Liu, C. Lee et al., “Progress in the Production and Application of N-butanol as a Biofuel,” *Renewable and Sustainable Energy Reviews*, 15:4080–4106, 2011.
16. S. Kumar, J. H. Cho, J. Park, and I. Moon, “Advances in Diesel–alcohol Blends and Their Effects on the Performance and Emissions of Diesel Engines,” *Renewable and Sustainable Energy Reviews* 22:46–72, 2013.

17. X. Gu, G. Li, X. Jiang, Z. Huang et al., "Experimental Study on the Performance of and Emissions from a Low-speed Light-duty Diesel Engine Fueled with n-Butanol–Diesel and Isobutanol–Diesel Blends," *Proc IMechE Part D: J Automobile Engineering* 227(2):261–271, 2013, doi:10.1177/0954407012453231.
18. M. Lapuerta, R. Garcia-Contreras, J. Campos-Fernandez, and M. Pilar Dorado, "Stability, Lubricity, Viscosity, and Cold-Flow Properties of Alcohol-Diesel Blends," *Energy & Fuels*, 24:4497–4502, 2010.
19. B. Heuser, T. Laible, M. Jakob, F. Kremer et al., "C8-Oxygenates for Clean Diesel Combustion," *SAE Technical Paper* 2014-01-1253, 2014, doi:10.4271/2014-01-1253.
20. J. Campos-Fernandez, J. M. Arnal, J. Gomez, N. Lacalle et al., "Performance Tests of a Diesel Engine Fueled with Pentanol/Diesel Fuel Blends," *Fuel*, 107:866–872, 2013.
21. J. Trost, L. Zigan, and A. Leipertz, "Quantitative Vapor Temperature Imaging in DISI-Sprays at Elevated Pressures and Temperatures using Two-Line Excitation Laser-Induced Fluorescence," *Proc. Combust. Inst.*, 34(2):3645–3652, 2013.
22. Morone and R.A. Pandey, "Lignocellulosic Biobutanol Production: Gridlocks and Potential Remedies," *Renewable and Sustainable Energy Reviews*, 37:21–35, 2014.
23. Directive 2009/28/EC of the European Parliament and of the Council, 2009.
24. C. D. Rakopoulos, K. A. Antonopoulos, and D. C. Rakopoulos, "Experimental Heat Release Analysis and Emissions of a HSDI Diesel Engine Fueled with Ethanol-Diesel Fuel Blends," *Energy* 32(10):1791–1808, 2007.
25. N. Noguchi, H. Terao, and C. Sakata, "Performance Improvement by Control of Flow Rates and Diesel Injection Timing on Dual-Fuel Engine with Ethanol," *Bioresour. Technol.*, 56(1):35–39, 1996.
26. H. Liu, X. Wang, Z. Zheng, J. Gu, H. Wang et al., "Experimental and Simulation Investigation of the Combustion Characteristics and Emissions using n-Butanol / Biodiesel Dual-Fuel Injection on a Diesel Engine," *Energy*, 74:741–752, 2014.
27. X. Han, M. Zheng, and J. Wang, "Fuel Suitability for Low Temperature Combustion in Compression Ignition Engines," *Fuel*, 109:336–349, 2013.
28. B. S. Chauhan, N. Kumar, S. S. Pal, and Y. Du Jun, "Experimental Studies on Fumigation of Ethanol in a Small Capacity Diesel Engine," *Energy*, 36(2):1030–1038, 2011.
29. Z. H. Zhang, K. S. Tsang, C. S. Cheung, T. L. Chan et al., "Effect of Fumigation Methanol and Ethanol on the Gaseous and Particulate Emissions of a Direct-Injection Diesel Engine," *Atmos. Environ.*, 45(11):2001–2008, 2011.
30. N. C. Surawski, B. Miljevic, B. A. Roberts, R. L. Modini et al., "Particle Emissions, Volatility, and Toxicity from an Ethanol Fumigated Compression Ignition Engine," *Environ. Sci. Technol.*, 44(1):229–235, 2010.

31. Z. Chen, J. Liu, Z. Wu, and C. Lee, "Effects of Port Fuel Injection (PFI) of n-Butanol and EGR on Combustion and Emissions of a Direct Injection Diesel Engine," *Energy Convers. Manag.*, 76:725–731, 2013.
32. R. Michikawauchi, S. Tanno, Y. Ito, and M. Kanda, "Combustion Improvement of Diesel Engine by Alcohol Addition - Investigation of Port Injection Method and Blended Fuel Method," SAE paper 2011-01-0336, 2013.
33. M. Abu-Qudais, O. Haddad, and M. Qudaisat, "The Effect of Alcohol Fumigation on Diesel Engine Performance and Emissions," *Energy Convers. Manag.*, 41(4):389–399, 2000.
34. Z. Şahin, O. Durgun, and O. N. Aksu, "Experimental Investigation of n-Butanol/Diesel Fuel Blends and n-Butanol Fumigation – Evaluation of Engine Performance, Exhaust Emissions, Heat Release and Flammability Analysis," *Energy Convers. Manag.*, 103:778–789, 2015.
35. J. Campos-Fernández, J. Arnal, J. Gómez, and M. Pilar Dorado, "A Comparison of Performance of Higher Alcohols/diesel Fuel Blends in a Diesel Engine," *Applied Energy*, 95: 267–275, 2012.
36. Ö. Can, I. Çelikten, and N. Usta, "Effects of Ethanol Addition on Performance and Emissions of a Turbocharged Indirect Injection Diesel Engine Running at Different Injection Pressures," *Energy Convers. Manag.*, 45(15–16):2429–2440, 2004.
37. D. C. Rakopoulos, C. D. Rakopoulos, R.G. Papagiannakis, and D.C. Kyritsis, "Combustion Heat Release Analysis of Ethanol or n-Butanol Diesel Fuel Blends in Heavy-Duty DI Diesel Engine," *Fuel*, 90:1855–1867, 2011.
38. Armas, R. García-Contreras, and Á. Ramos, "Pollutant Emissions from Engine Starting with Ethanol and Butanol Diesel Blends," *Fuel Process. Technol.*, 100:63–73, 2012.
39. Armas, R. García-Contreras, and Á. Ramos, "Pollutant Emissions from New European Driving Cycle with Ethanol and Butanol Diesel Blends," *Fuel Process. Technol.*, 122:64–71, 2014.
40. V. Soloiu, M. Duggan, S. Harp, B. Vlcek, and D. Williams, "PFI (port fuel injection) of n-Butanol and Direct Injection of Biodiesel to Attain LTC (Low-Temperature Combustion) for Low-Emissions Idling in a Compression Engine," *Energy*, 52:143–154. 2013.
41. M. Ickes, S. V Bohac, and D. N. Assanis, "Effect of Fuel Cetane number on a Premixed Diesel Combustion Mode," *Int. J. Engine Res.*, 10(4):251–263, 2009.
42. N. Ladommatos, M. Parsi, and A. Knowles, "The Effect of Fuel Cetane Improver on Diesel Pollutant Emissions," *Fuel*, 75(1):8–14, 1996.

43. L. J. Cunningham, T. J. Henly, and A. M. Kulinowski, "The Effects of Diesel Ignition Improvers In Low-Sulfur Fuels on Heavy-Duty Diesel Emissions," SAE Paper, 902173, 1990.
44. X. Li, W. L. Chippior, and Ö. L. Gülder, "Effects of Fuel Properties on Exhaust Emissions from the Latest Light-Duty DI Diesel Engine," SAE Paper 962116, 1996.
45. Y. Kidoguchi, C. Yang, R. Kato, and K. Miwa, "Effects of Fuel Cetane Number and Aromatics on Combustion Process and Emissions of a Direct-Injection Diesel Engine," JSAE Rev., 21:469–475, 2000.
46. L. Xing-Cai, Y. Jian-Guang, Z. Wu-Gao, and H. Zhen, "Effect of Cetane Number Improver on Heat Release Rate and Emissions of High Speed Diesel Engine Fueled with Ethanol-Diesel Blend Fuel," Fuel, 83(14–15):2013–2020, 2004.
47. X. C. Lü, J. G. Yang, W. G. Zhang, and Z. Huang, "Improving the Combustion and Emissions of Direct Injection Compression Ignition Engines using Oxygenated Fuel Additives Combined with a Cetane Number Improver," Energy and Fuels, 19(5):1879–1888, 2005.
48. Y. İcingür and D. Altıparmak, "Effect of Fuel Cetane Number and Injection Pressure on a DI Diesel Engine Performance and Emissions," Energy Convers. Manag., 44(3):389–397, 2003.
49. G. Knothe, A. C. Matheaus, and T. W. Ryan, "Cetane Numbers of Branched and Straight-Chain Fatty Esters Determined in an Ignition Quality Tester," Fuel, 82(8):971–975, 2003.
50. G. Knothe, "Dependence of Biodiesel Fuel Properties on the Structure of Fatty Acid Alkyl Esters," Fuel Process. Technol., 86(10):1059–1070, 2005.
51. Sudholt, L. Cai, J. Heyne, F. M. Haas et al., "Ignition Characteristics of a Bio-Derived Class of Saturated and Unsaturated Furans for Engine Applications," Proc. Combust. Inst., 35(3):2957–2965, 2015.
52. Ramadan, G. Webster, L. Menard, A. Wilcox et al., "Ignition Quality Tester ( IQT TM ) Precision Improvements from Using the Totally Automated Laboratory Model ( TALM ) Technology : Technology Update , Part-2 : Mini Inter- Laboratory Study Using the IQT TM -TALM," SAE Technical Paper 2015-01-0805, 2015
53. L. N. Allard, G. D. Webster, T. W. Ryan, G. Baker et al., "Analysis of the Ignition Behaviour of the ASTM D-613 Primary Reference Fuels and Full Boiling Range Diesel Fuels in the Ignition Quality Tester ( IQT ) - Part III," SAE Paper, 1999–01–3591, 1999.
54. S. Bezergianni and A. Dimitriadis, "Comparison between Different Types of Renewable Diesel," Renew. Sustain. Energy Rev., 21:110–116, 2013.
55. P. Ghosh and S. B. Jaffe, "Detailed Composition-Based Model for Predicting the Cetane Number of Diesel Fuels," Ind. Eng. Chem. Res., 45:346–351, 2006.

- 
56. Eric Sattler, "Comparing Methods to Determine Cetane Ratings of Fuel Blends," U.S. Army Tank Automotive Research, Development and Engineering Center, U.S. Army Research, Development and Engineering Command. 2009.
  57. Z. Xiao, N. Ladommatos, and H. Zhao, "The Effect of Aromatic Hydrocarbons and Oxygenates on Diesel Engine Emissions," *Proc. Inst. Mech. Eng. Part D-Journal Automob. Eng.*, 214(D3):307–332, 2000.
  58. D.C. Rakopoulos, C.D. Rakopoulos, E.G. Giakoumis, A.M. Dimaratos et al., "Effects of Butanol–Diesel Fuel Blends on the Performance and Emissions of a High-speed DI Diesel Engine," *Energy Conversion and Management* 51:1989–1997, 2010.
  59. E. Sukjit, J. M. Herreros, K. D. Dearn, R. García-Contreras et al., "The Effect of the Addition of Individual Methyl Esters on the Combustion and Emissions of Ethanol and Butanol-Diesel Blends," *Energy*, 42,(1):364–374, 2012.
  60. G. Valentino, S. Merola, L. Marchitto, and C. Tornatore, "Butanol-Diesel Blend Spray Combustion Investigation by UV-Visible Flame Emission in a Prototype Single Cylinder Compression Ignition Engine," *SAE Int. J. Engines*, 8(5):2015–24–2435, 2015.
  61. H. Wu, K. Nithyanandan, J. Zhang, Y. Lin et al., "Impacts of Acetone – Butanol – Ethanol ( ABE ) Ratio on Spray and Combustion Characteristics of ABE – Diesel Blends," *Appl. Energy*, 149:367–378, 2015.
  62. Q. Zhang, M. Yao, Z. Zheng, H. Liu et al. "Experimental Study of n-Butanol Addition on Performance and Emissions with Diesel Low Temperature Combustion." *Energy*, 47:515–521, 2012.
  63. M. Yao, H. Wang, Z. Zheng, Y. Yue, "Experimental Study of n-Butanol Additive and Multi-Injection on HD Diesel Engine Performance and Emissions." *Fuel*, 89:2191–2201, 2010.
  64. C. D. Rakopoulos, D. C. Rakopoulos, E. G. Giakoumis, and D. C. Kyritsis, "The Combustion of n-Butanol/Diesel Fuel Blends and its Cyclic Variability in a Direct Injection Diesel Engine," *Proc. Inst. Mech. Eng. Part A J. Power Energy*, 225(3):289–308, 2011.
  65. G. Valentino, F. E. Corcione, S. E. Iannuzzi, and S. Serra, "Experimental Study on Performance and Emissions of a High Speed Diesel Engine Fuelled with n-Butanol Diesel Blends under Premixed Low Temperature Combustion," *Fuel*, 92(1):295–307, 2012.
  66. G. Valentino, F. E. Corcione, S. Iannuzzi, and U. Cagliari, "An Experimental Analysis on Diesel / n-Butanol Blends Operating in Partial Premixed Combustion in a Light Duty Diesel Engine," *SAE Paper* 2012-01-1127, 2012.

67. S. Berkous, "Using A Constant Volume Combustion Chamber Analyzer For Predicting Derived Cetane Number Of Aviation Turbine Fuels," IASH Paper, 2009.
68. S. Kumar, J. H. Cho, J. Park, and I. Moon, "Advances in Diesel-Alcohol Blends and their Effects on the Performance and Emissions of Diesel Engines," *Renew. Sustain. Energy Rev.*, 22:46–72, 2013.
69. G. Woschni, "A Universally Acceptable Equation for the Instantaneous Heat Transfer Coefficient in the Internal Combustion Engine," SAE Tech. Pap. 670931, 1967.
70. Economic Commission for Europe, "Proposal for Draft Amendment 3 to Global Technical Regulation (gtr) No. 4: Test Procedure for Compression-Ignition (C.I.) Engines and Positive-Ignition (P.I.) Engines Fuelled with Natural Gas (NG) or Liquefied Petroleum Gas (LPG) with Regard to the Emission of Pollutants," 2014.
71. Commission Directive 2005/78/EC, 2005.
72. H. Ghiassi, P. Toth, and J. Lighty, "Sooting Behaviors of n-Butanol and n-Dodecane Blends," *Combustion and Flame* 161(3):671–679, 2012.